

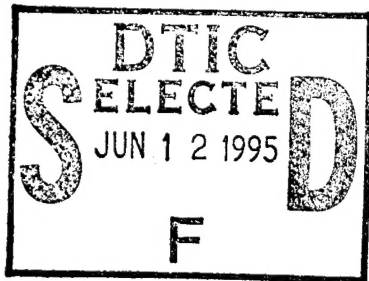
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THE STUDY OF TOUGHENING BISMALEIMIDE RESIN
-- THE TOUGHENING EFFECT OF RUBBER

by

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THE STUDY OF TOUGHENING BISMALEIMIDE RESIN
-- THE TOUGHENING EFFECT OF RUBBER

/71*

Lan LiWen¹ Liu Linan²

Abstract

We have studied the toughening effect of epoxylrandomed butadien-acrylonitrile rubber on 4, 4'-bismaleimicphenyl-methane/E-51 epoxy resin/4,4'-diaminodiphenylsulfone system. We looked at the effect of rubber content on the mechanical properties of cure resin, the process of forming two phase structure and morphology of fracture. We also analyzed multi-image craze theory with our data.

Key words: bismaleimide, rubber, two phase structure, toughening, morphology of fracture.

Epoxy resin(EP) is often used to improve the property of bismaleimide(BMI) in conjunction with DA. DA is not only the expansion reagent of BMI, but also a polymerizing agent of EP, therefore, a complicated network can be formed within BMI/EP/DA system. This system has the very useful industrial nature of EP, and the heat resistance of BMI. It is a very important basic composite material and gluing reagent.

However, BMI/EP/DA resin system remains to be further toughened. Some commonly used toughening reagents are functional groups containing rubber. At present, the theory on EP toughening by rubber is well taken, but hardly any study has been done on the theory on BMI resin toughening by rubber. We studied the toughening effect of rubber on

* Numbers in margins indicate foreign pagination.
Commas in numbers indicate decimals.

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BMI/EP/DA, and forming process of two phase structure and the theory on resin toughening by rubber.

1. EXPERIMENT

1.1 Making of the resin mold

The formulation of resin is listed in table 1. Components A and C are mixed and melted. After B and D are added in, they are evenly mixed and poured into a preheated mold. Subsequently, they are vacuum degassed and allowed to polymerize at 150°C/1h+180°C/1h+200°C/2h.

1.2 Assessment of resin properties

The solidifying time of the resin is determined by electric thermal board, it is defined as the point when stickiness is lost. The DSC analysis is conducted at CDR-1 type differential thermal analyzer in the presence of N₂, the heating rate 10°C/min.

The mechanical properties of the cured resin were assessed by national standards. Elongation, bending, and bombardment were carried out on Instron 9600 and XCZ-400 machines. The HDT was tested by our self-designed equipment based on GB1634-79. The fractured side was used as carbon film model and coated with gold. Subsequently, it was examined with HY-800 transmission microscope.

Tab. 1 Formulation of resins (PHR)

Formulation	Resin system			
	I	II	III	IV
(A) 4,4' -Bismaleimidiphenylmethane	50	50	50	50
(B) Epoxy resin E-51	50	50	50	50
(C) 4,4' -Diaminodiphenylsulfone(DDS)	15	15	15	15
(D) Croxylrandomed butadien-acrylonitrile rubber (CRBN)	0	10	20	30

2. Results and Discussion

In order to assess the toughening effect of CRBN on BMI/E-51/DDS system, the properties of cured resin were measured as they were shown in Table 2 and fig. 1-5.

Tab. 2 Properties of cured resins

Properties	Resin system			
	I	II	III	IV
Tensile strength/MPa	56.8	63.8	71.8	70.8
Tensile modulus/GPa	3.96	3.08	3.27	3.21
Tensile elongation/%	2.0	2.2	2.6	2.4
Fracture work/kJ·m ⁻²	29.2	34.3	46.6	42.6
Flexural strength/MPa	116.7	119.5	140.7	
Flexural modulus/GPa	2.73	2.55	2.40	
Impact strength/kJ·m ⁻²	7.1	11.4	12.2	
HDT/°C	260	228	192	148

As it was shown in Table 2, the tensile strength and elongation increase as CRBN increases. At CRBN 20 phr, they are reaching maxima while tensile modulus and HDT decrease. At CRBN 20 phr, there is considerable amount of toughening effect. This is similar to the toughening effect of rubber on resin.

2.1 The formation of two phase structure of resin

According to the theory on rubber toughening on resin, the toughening effect correlates to two phase structure which results from resin polymerization. By observing the fracture point of cured resin in different solidifying stages under electron microscope, we can monitor the formation of this polymer structure. For complex resin systems, the formation of polymerizing structure is contingent upon the competition of different reactions of various components. For BMI/E-51/DDS/CRBN resin system, the major reactions in polymerization are (1)epoxy and amino group; (2) epoxy and carbonyl group of CRBN; (3) the michael reaction of bismaleimide and amino group; (4) the self polymerizing reaction of BMI. (1) and (4) are major reactions that contribute to the polymerization.

Tab. 3 Gel time and cure exothermic peak temperature of resin and it's formulations

System	$T_{\text{gel}}/^{\circ}\text{C}$	$GT/^{\circ}\text{C}$	Exothermic peak temperature $/^{\circ}\text{C}$		
			T_1	T_2	T_3
BMI/DDS	150	>300	238	278	300
	180	137			
E-51/DDS	150	114	180	230	280
	180	48			
BMI/E-51/DDS/CRBN	150	137	175	233	290
	180	73			
BMI			235	273	300

It was shown in the experiment, that the reaction rate differs from one reaction to the other. The reaction peak temperature and gel time(GT) of BMI/E-51/DDS/CRBN are listed in Table 3. Judging from the data in Table 3, AE-51 and DDS have lowest GT; while BMI and DDS have longest GT. This reflects the low reaction rate in the reaction between BMI and DDS and self polymerizing reaction of them. The gel

time(GT) of BMI/E-51/DDS/CRBN is dependent on the reaction between E-51 and DDS. This is confirmed by the measured exothermic peak temperature of various systems.

When BMI/E-51/DDS/CRBN resin is partially cured at 150°C/2h, the formation of big particles with a diameter 0.5-4 μm is visible(scattering phase, fig. 1).

Judging from GT data (Table 3), when cured at 150°C/2h, EP will turn into gel while BMI still remains as liquid, therefore scattering phase can be regarded as EP rich phase(CRBN has yet precipitated). When cured at 150°C/1h, the numbers and diameter of these particles increase considerably (fig.2). This is due to the gelatinization of more EP and their precipitation forms contiguous phase.

By further increasing the cure temperature, i.e. cure at 150°C/4h plus 180°C/4h, large particles will disappear, particles with 0.1 -1.0 μm diameter will emerge. Their size and number remain unchanged even under extended cure at 200°C/2h (Fig.3). When cured at 150°C/4h plus 180°C/4h, cross reaction will take place in BMI, in which BMI in contiguous phase reacts with the one in EP rich phase and crossing net. As a result, border lines among previous phases will disappear. At the same time, CRBN precipitates out and forms new scattering phase, i.e. the particles in fig.3. In the contiguous phase, EP rich and BMI rich regions will form. Therefore, the two phase structure of the resin will have fundamental changes in the later stage of resin cure. This ultimately results in formation of the scattering phase which is CRBN based stable polymer structure.

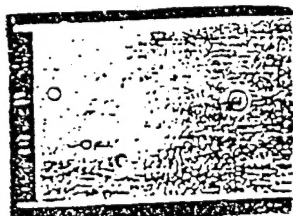


Fig. 1 SEM micrograph of resin system II cured by 150°C/2h



Fig. 2 SEM micrograph of resin system II cured by 150°C/4h

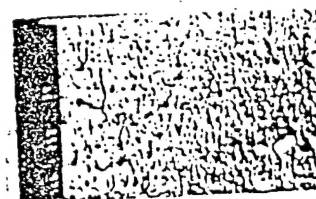


Fig. 3 SEM micrograph of resin system II cured by 150°C/4h + 180°C/4h

2.2 The mechanism of toughening by resin

The number and size of rubber particles in resin in the polymerized state is dependent on CRBN content. When CRBN is 10 phr, the diameter of rubber particles is in the range of 0.1-0.8 μm , mostly around 0.2-0.4 μm . When CRBN approaches 20 phr, the range of diameter of particles become 0.1-1.0 μm , majority of them are in the range of 0.4-1.0 μm , the number of these particles will also increase.

Resins with different content of rubber tend to have different fracture morphology. The "river line" in fracture surface of resin system I is very straight (see fig.4), indicating a smooth expansion of the fracture. This is a typical abrupt fracture. Therefore, resin system I has very low flexural strength, fracture elongation rate.

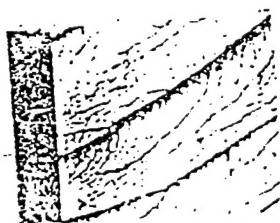


Fig. 4 Fracture morphology of resin system I ($\times 8000$)



Fig. 5 Fracture morphology of resin system I ($\times 5000$)



Fig. 6 "river line" in fracture surface for resin system I ($\times 12000$)

Resin system III (contains 10 phr CRBN) has similar fracture morphology as fig.4, i.e. abrupt fracture. Further examination under high magnification (fig.6) shows some cured "river line" on part of the fracture surface. Rubber particles which are lined at the edge of the fracture blocked the expansion of the fracture. This is comparable to the role of nails. When the front edge of fracture meets rubber particles, the front edge will be blunted; At the same time, gel particles will stick to the contiguous phase strongly, this leads to detour of the rubber particles by the front edge in order to continue expansion. As a result,

the trapped front edge will be forced to bend to form arches by the front edge, which will lead to further bending and elongation and higher fracture work. Despite the tendency of resin system II to be abrupt fracture, overall the rubber particles in some localized areas have a toughening effect due to the "nailing" effect of the fracture front edge.

Fracture morphology of resin system III is shown in fig.7. It is very different from the ones of resin system I and II. The fish scale like morphology of the fracture is similar to the one of toughened epoxy resin. Further magnification shows that there are gel particles in these fish scales. There are lots of micro-fractures around the gel particles, suggesting the gel particles play some role of magnet.



Fig. 7 Fracture morphology of resin system III ($\times 4000$)



Fig. 8 Fracture morphology of resin system III, It appears that the secondary fracture is initiated by rubber particles ($\times 12000$)

The fish scale morphology is a typical fracture morphology that is associated with rubber toughened by fragile resin. The fish scales and many gel particles induced cracking lines which converge and expand to form fractures. This formation process is addressed in reference (5).

Based on the above discussion, we can see that when the rubber content in resin is high (20 phr for resin systems),

the size of gel particles is big enough to induce cracking lines. The flexural strength can be improved drastically.

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